

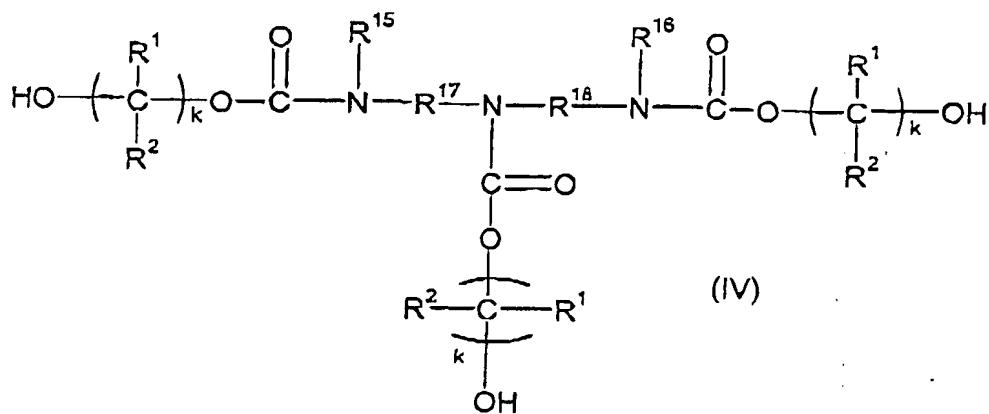
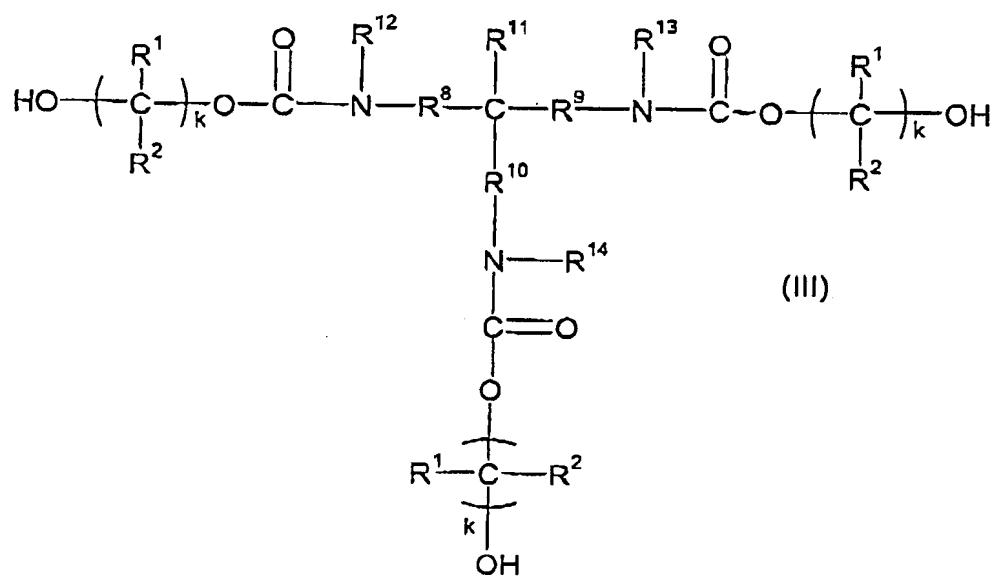
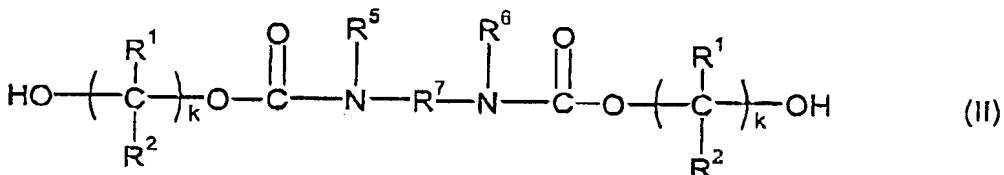
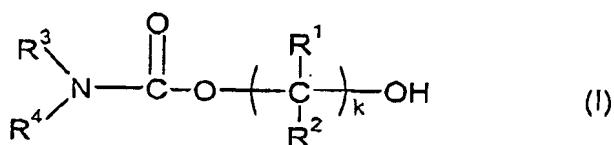
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## Claims

1. Process for producing urethane (meth)acrylates which comprises the reaction of (a) at least one hydroxyalkyl carbamate of formula (I), (II), (III), (IV), (V), (VI) or (VII)

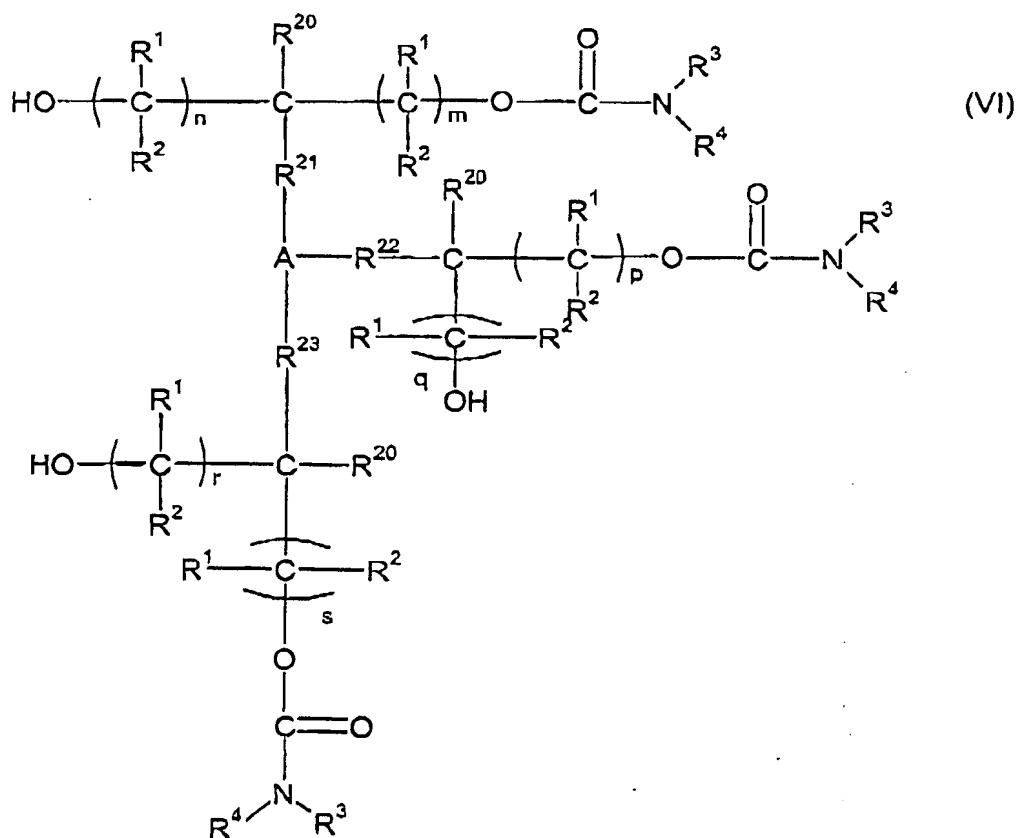
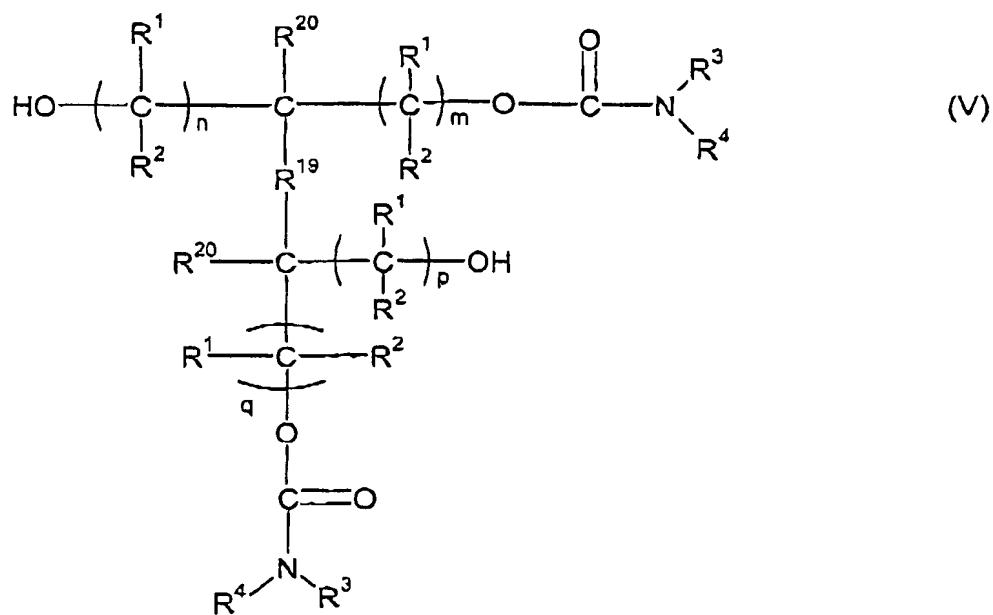


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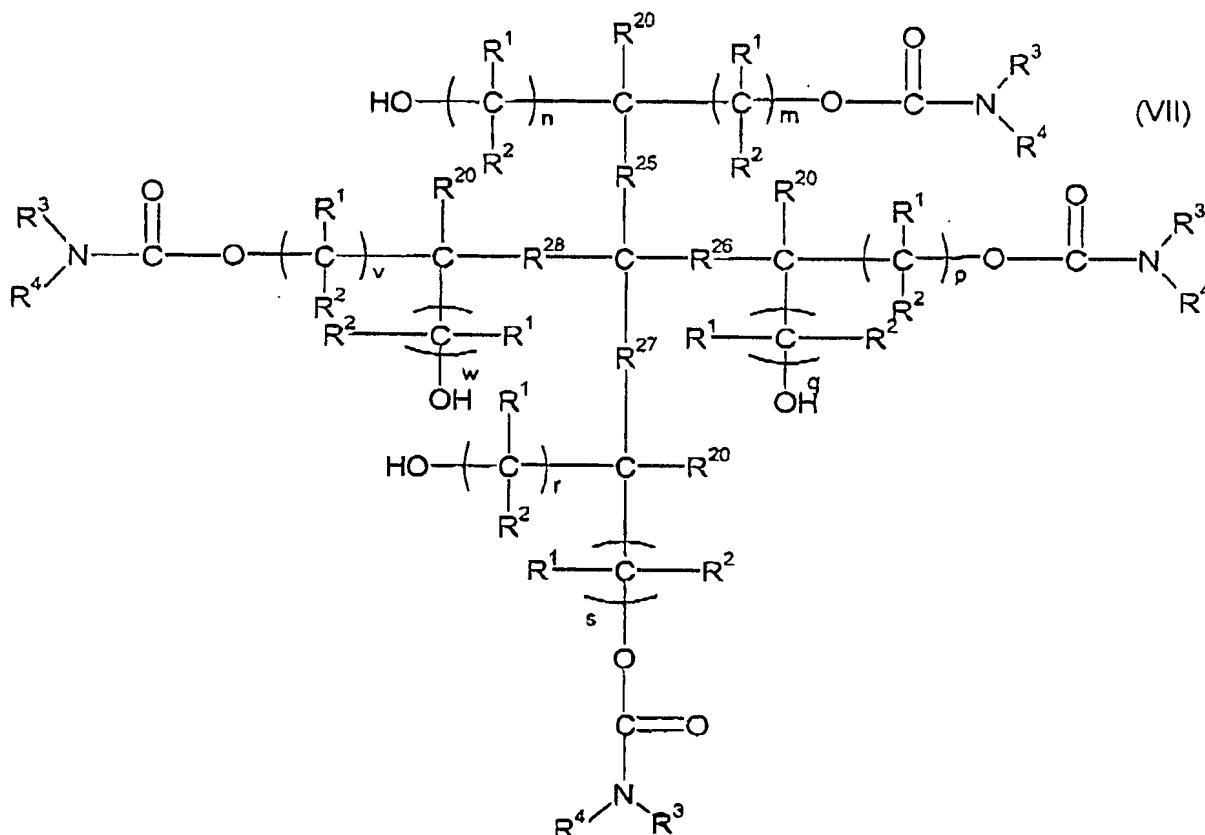
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wherein

$$k \geq 2$$

$n = 0 \text{ to } 2$

5 m = 0 to 2

$$n+m \geq 1$$

$p = n \text{ or}$

$p = \text{norm}$ ,  $q = \text{norm}$ ,  $r = \text{norm}$ ,  $s = \text{norm}$ ,  $v = \text{norm}$ ,  $w = \text{norm}$

$$(p+q) = (r+s) = (v+w) = (n+m)$$

each  $R^1$ , each  $R^2$ , each  $R^{20}$  is, independently, chosen from the group of

10

-hydrogen,

• halogen,

• hydroxy,

alkyl, optionally substituted by hydroxy; halogen; aryl and/or aryl substituted by hydroxy, halogen or alkyl; and optionally containing from 1 to 8 ether bridges.

15

· alkenyl, optionally substituted by hydroxy; halogen; aryl and/or aryl substituted by hydroxy, halogen or alkyl; and optionally containing from 1 to 8 ether bridges

• aryl, optionally substituted by hydroxy; halogen; alkyl; alkyl substituted by hydroxy, halogen and/or aryl; and/or alkyl containing from 1 to 8 ether bridges

$R^3$  is an alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 20 ether bridges and/or from 1 to 3 tertiary amine bridges.

$R^4, R^5, R^6, R^{12}, R^{13}, R^{14}, R^{15}$  and  $R^{16}$  are independently chosen from the group of

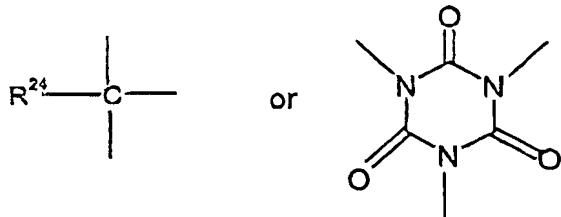
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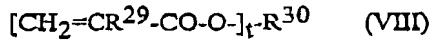
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- hydrogen, and
  - alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges,
  - with the proviso that, respectively, R<sup>3</sup> and R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup>, R<sup>12</sup> and/or R<sup>13</sup> and/or R<sup>14</sup>, R<sup>15</sup> and R<sup>16</sup> may be linked together in order to form a ring,
- 5 R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>17</sup> and R<sup>18</sup> are, independently, chosen from alkylene, alkenylene, arylene and aralkylene chains which may contain from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges,
- 10 R<sup>11</sup> is hydrogen or alkyl;
- R<sup>19</sup>, R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup>, R<sup>25</sup>, R<sup>26</sup>, R<sup>27</sup> and R<sup>28</sup>, are, independently, chosen from alkylene, alkenylene, arylene and aralkylene chains which may contain from 1 to 20 ether bridges, from 1 to 4 tertiary amine bridges, from 1 to 4 -CO- bridges and/or from 1 to 4 -O-CO- bridges;

A is

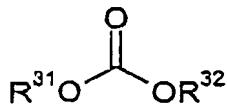
15 wherein R<sup>24</sup> is hydrogen or alkyl;

(b) at least an (meth)acrylate of formula (VIII)

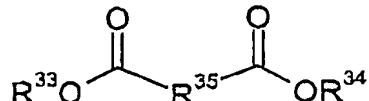


wherein R<sup>29</sup> is hydrogen or methyl, and R<sup>30</sup> represents an alkyl, optionally substituted by hydroxy, which may contain from 1 to 10 ether bridges group, from 1 to 10 -O-CO-O- bridges and/or from 1 to 10 -O-CO- bridges; t ≥ 1; and

(c) at least one carbonate of formula (IX) and/or a diester of formula (X)



(IX)



(X)

wherein

each R<sup>31</sup>, each R<sup>32</sup>, each R<sup>33</sup>, each R<sup>34</sup> is, independently, chosen from the group of alkyl and aryl, R<sup>35</sup> is alkylene, alkenylene or arylene; and

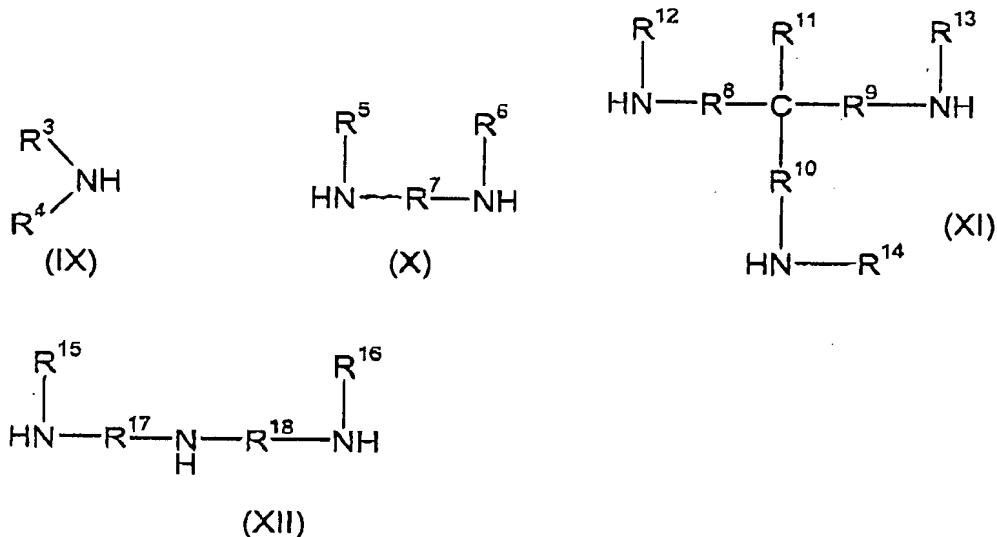
(d) optionally, at least one polyol different from the hydroxyalkyl carbamates (a); in the presence of at least one transesterification catalyst

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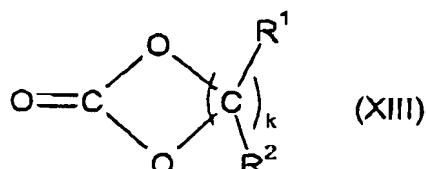
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2. The process according to claim 1, wherein the hydroxyalkyl carbamates of formula (I), (II), (III) and (IV) are obtained by reacting amines of, respectively, formula (IX), (X), (XI) and (XII)

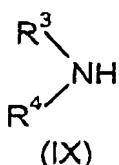


wherein R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup>, R<sup>14</sup>, R<sup>15</sup>, R<sup>16</sup>, R<sup>17</sup> and R<sup>18</sup>, are defined as in claim 1, with a cyclic carbonate of formula (XIII)



wherein  $R^1$ ,  $R^2$  and  $k$  are defined as in claim 1.

10 3. The process according to claim 1, wherein the hydroxyalkyl carbamates of formula (V), (VI) and (VII) are obtained by reacting an amine of formula (IX)

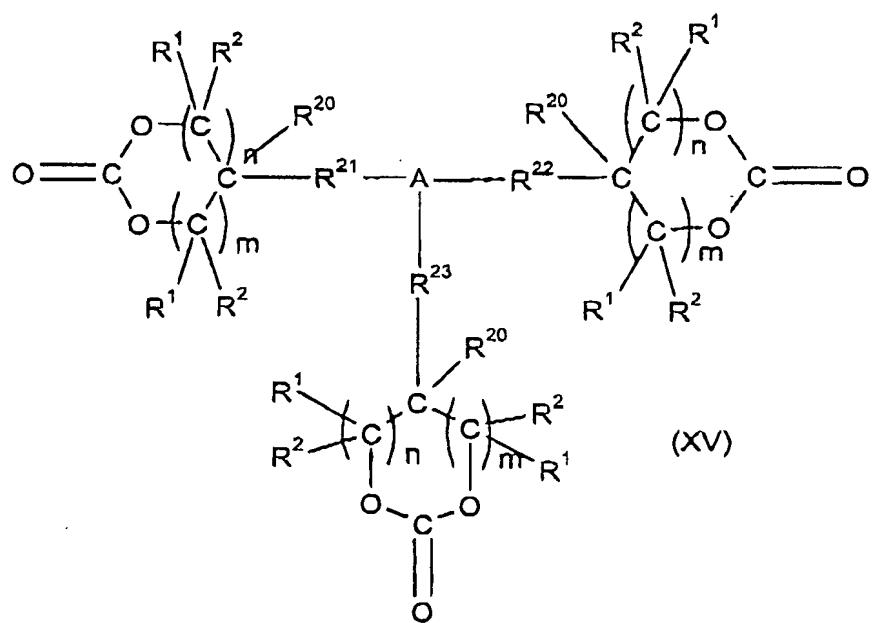
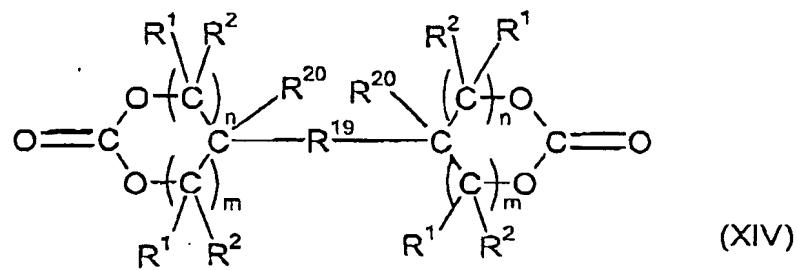


15 wherein  $R^3$  and  $R^4$  are defined as in claim 1, with, respectively, a cyclic carbonate of formula (XIV), (XV) and (XVI)

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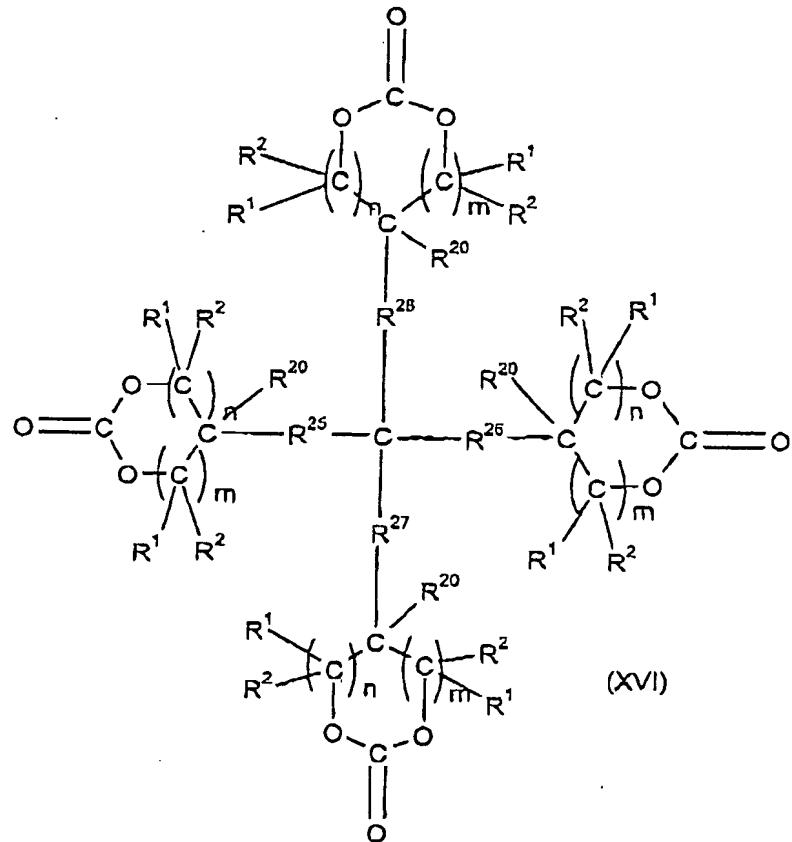
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wherein  $R^1, R^2, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28}, A, n$  and  $m$  are defined as in claim 1.

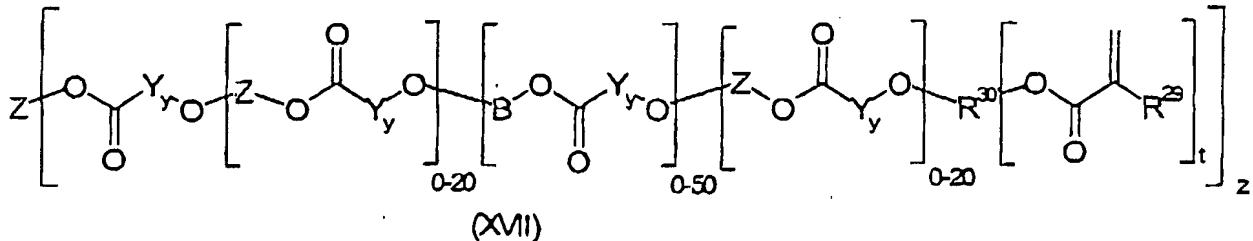
4. The process according to any of claims 1 to 3, wherein the transesterification catalyst is selected from organotitanates, organozirconates and organotin catalysts.
  5. The process according to 4, wherein the transesterification catalyst is an alkyltitanate wherein each alkyl, independently, comprises from 2 to 8 carbon atoms or an alkylzirconate wherein each alkyl, independently, comprises from 2 to 8 carbon atoms or a zirconium 1,3-diketone chelate or a mixture thereof.
  - 10 6. The process according to any of claims 1 to 5, wherein the transesterification reaction is conducted in the presence of at least one polymerization inhibitor.
  7. The process according to any of claims 1 to 6, wherein the temperature during the transesterification reaction is at most 120°C.
  - 15 8. The process according to any of claims 1 to 7, wherein the weight ratio of catalyst to the generated methane (meth)acrylate is from 0.001 to 0.2.
  9. The process according to any of claims 1 to 8, wherein  $k=2$  or  $3$  and  $n+m, p+q, r+s, v+w = 1$ .
  10. The process according to any of claims 1 to 9, wherein in formula (I), (II), (III) and (IV) one of the  $R^1$  substituents is chosen from the group of hydrogen, methyl, ethyl, hydroxymethyl, chloromethyl, allyloxymethyl, the  $R^2$  substituent present on the same substituent as said  $R^1$  substituent is chosen from hydrogen and methyl, and all other  $R^1$  and  $R^2$  substituents are hydrogen.

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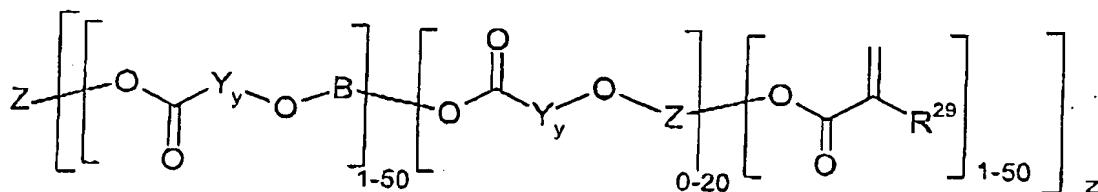
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11. The process according to any of claims 1 to 9, wherein in formula (V), (VI) and (VII) each  $R^1$ , each  $R^2$  and each  $R^{20}$  is hydrogen.
12. The process according to any of claims 1 to 11, wherein in formula (I), (V), (VI) and (VII) and (IX)  $R^4$  is hydrogen and  $R^3$  is an alkyl comprising at least 3 carbon atoms and substituted by at least one hydroxy and optionally containing one or two ether bridges.
13. The process according to any of claims 1 to 12, wherein in formula (VIII)  $t$  is 1 and wherein  $R^{30}$  is an alkyl comprising from 1 to 6 carbon atoms or an alkyl substituted by at least one hydroxy group, and which may contain from 1 to 10 ether bridges group, from 1 to 10 -O-CO-O- bridges or from 1 to 10 -O-CO- bridges.
14. The process according to any of claims 1 to 13, wherein in the carbonates of formula (IX)  $R^{31}$  and  $R^{32}$  are chosen from the group of alkyl comprising from 1 to 4 carbon atoms and from phenyl.
15. The process according to any of claims 1 to 14, wherein in the diesters of formula (X)  $R^{33}$  and  $R^{34}$  are chosen from the group of alkyl comprising from 1 to 6 carbon atoms and from phenyl, and wherein  $R^{35}$  is an alkylene or alkenylene comprising from 1 to 10 carbon atoms or phenylene.
16. The process according to any of claims 1 to 15, wherein the polyol (d) responds to formula  $B-(OH)_x$  wherein  $x$  is an integer from 1 to 6 and  $B$  represents an alkyl or alkenyl optionally containing from 1 to 100 ether bridges, -CO-O- bridges, -CO- bridges and/or -O-CO-O- bridges and/or containing one or more -COOH, -SO<sub>3</sub>H and/or -PO<sub>4</sub>H groups.
17. The process according to claim 16, wherein the polyol (d) is chosen from ethylene glycol, propyleneglycol, 1,4-butanediol, 1,5-pentanediol, neopentylglycol, 1,6-hexanediol, diethyleneglycol, triethyleneglycol, dipropyleneglycol, tripropyleneglycol, cyclohexanedimethanol, dimethylolpropionic acid, trimethylolpropane, pentaerythritol and macrodiols such as polyetherdiols, polyesterdiols, polycarbonatediols, polystercarbonatediols, polybutadienediol, acrylic diols, and their mixtures.
18. The process according to any of claims 1 to 17, wherein the equivalent ratio of (meth)acrylate of formula (VIII) to hydroxyalkyl carbamate is from 0.01 to 7.
19. The process according to any of claims 1 to 18, wherein the equivalent ratio of carbonate (IX) and/or diester (X) to hydroxyalkyl carbamate is from 0.05 to 10.
20. The process according to any of claims 1 to 19, wherein the equivalent ratio of polyol (d) to hydroxyalkyl carbamate is from 0 to 50.
21. Urethane (meth)acrylates obtainable by the process according to any of claims 1 to 20.
22. Urethane(meth)acrylates responding to formula (XVII) and (XVIII)



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(XVIII)

wherein :

5 z is an integer from 1 to the number of OH groups present in the hydroxyalkyl carbamate of formula (I), (II), (III), (IV), (V), (VI) and/or (VII);

B is the residue of the polyol as defined in claim 16.

$R^{30'}$  represents an alkyl, which may contain from 1 to 10 ether bridges group, from 1 to 10  $-O-CO-O-$  bridges and/or from 1 to 10  $-O-CO-$  bridges.

10  $R^{29}$  and  $t$  are such as defined in claim 1.



and  $y$  is 0 or 1

23. Urethane(meth)acrylates according to claim 22, wherein  $\beta$  is 1.

hydroxylalkylcarbamates of formula (C) (T = 175-185°C)

15  $R^5$  and  $R^6$ , at least one of  $R^{12}$ ,  $R^{13}$  and  $R^{14}$ , and at least one of  $R^{15}$  and  $R^{16}$  is different from hydrogen.

24. Urethane(meth)acrylates according to claim 22, wherein Z is the residue of

hydroxyalkylcarbamates of formula (II) wherein R<sup>7</sup> is ethylene and R<sup>5</sup> and R<sup>6</sup> are methyl.

methoxyethylene, cyclohexyl-1,3-ene, cyclohexyl-1,4-ene, 1,4-bis(propoxyl-3-ene)butane, N,N-bis(trimethylene)methylamine, 3,6-dioxaoctylene, 3,8-dioxadodecylene, 4,7,10-trioxatridecyl

poly(oxytetramethylene), poly(oxypropylene) with 2 to 15 1,2-propylene oxide units, poly(oxypropylene-co-oxyethylene) with 2 to 15 propylene oxide and 2 to 15 ethylene oxide units.

25 26. Use of urethane (meth)acrylates according to any of claims 21 to 25 in a radiation curable composition.

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